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DEVELOPMENT OF A PROTOCOL FOR PREDICTING THE FATE OF HAZARDOUS CONTAMINANTS IN MUNICIPAL SEWAGE SYSTEMS

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Development of a Protocol for Predicting the Fate of Hazardous Contaminants in Municipal Sewage Systems

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Executive Summary

This report describes the background to, and incentives for, the development of a protocol or calculation procedure by which the fate of hazardous contaminants could be quantitatively assessed in municipal sewage collection and treatment systems. The state of scientific knowledge concerning the properties of hazardous chemical contaminants and their fate in laboratory, pilot and full scale treatment systems is reviewed. Particular emphasis is devoted to biodegradability. Several potential bench mark chemicals are identified. The current status of modelling in sewer systems and treatment plants is reviewed.

Studies are identified which, when successfully completed, could provide the knowledge base from which the proposed protocol could be developed. It is believed that within 2 years there could be in place a capability for estimating the fate of hazardous contaminants in municipal collection and treatment systems. This would form an invaluable component of the effort to reduce municipal discharges to the environment to acceptable levels as part of the overall MISA Strategy.

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J. Blackburn	University of Tennessee
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1. INTRODUCTION.

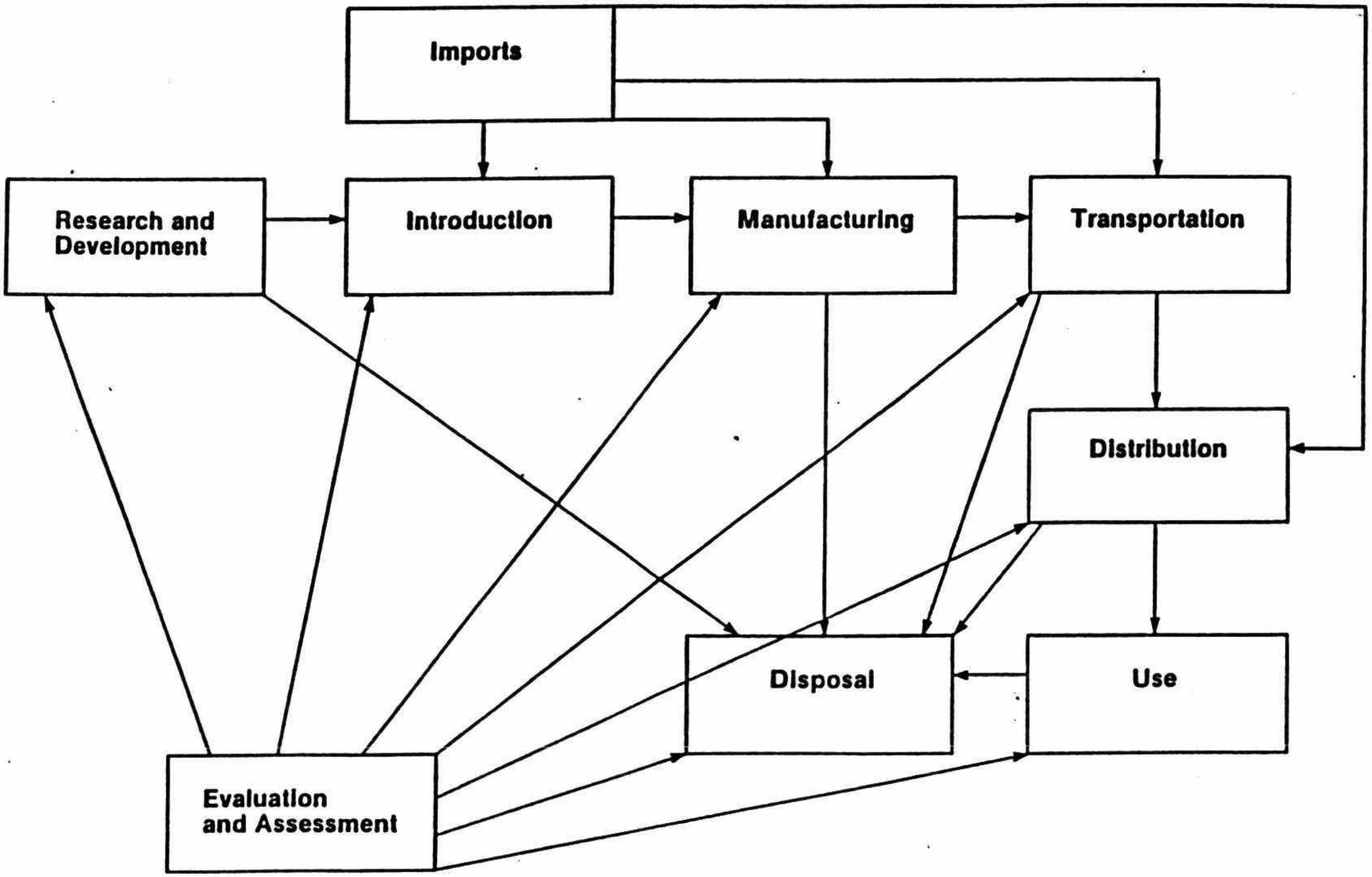
This report has been prepared jointly for the Ontario Ministry of Environment (MOE) Water Resources Branch and the Federal Department of Environment (DOE), Wastewater Technology Centre as a contribution to the Municipal-Industrial Strategy for Abatement (MISA) program which seeks in general to reduce or "virtually eliminate" the discharge of toxic contaminants in municipal and industrial discharges into Ontario's waterways (MOE 1986). Necessary components of this strategy are the development of a comprehensive data base of discharges and implementation of best available technologies economically achievable (BATEA) to reach desired effluent limits. A key concept in this approach is that information must be available to the regulatory agency concerning the fate of specific contaminants in the sewage collection and treatment systems. These fates vary greatly from chemical to chemical. Some chemicals pose little or no threat because they are rapidly degraded. Others may be rapidly volatilized in sewers and in treatment plants possibly resulting in local air pollution concerns. Some may sorb to sludges and receive further treatment such as anaerobic digestion or incineration. Others may become subject to dispersal as a result of land spreading. Others may pass into the receiving waters relatively unchanged. Clearly these chemicals present quite different problems and should receive quite different treatment or control approaches and priorities. Depending on their toxicity and persistence, some may merit outright banning of discharge, others may be acceptable in relatively large amounts.

But in most cases a judgement must be made of a tolerable discharge.

This report seeks to improve the decision-making process which is part of this judgement. The issue is complicated by the large, and increasing number of organic and inorganic chemicals which are used industrially and domestically and which have been observed in environmental media such as water, fish and air. The properties and fate of many of these chemicals are poorly understood. Regulatory agencies are thus placed in the difficult position of recommending and enforcing controls, often incurring expense and inconvience to the public and industry, about chemicals for which there is an acknowledged lack of understanding. Reference can be made to the MISA Policy & Program Statement (MOE 1986) and to other MISA documents including the response to public comments for further background and an outline of the proposed abatement strategy.

The broad issue of managing chemicals has been reviewed in the Environment Canada Report "From Cradle to Grave: A Management Approach to Chemicals" (Environment Canada 1986). This report provides an excellent overview of the life cycle approach in which the chemical is subject to scrutiny and possible control at all stages of its life from research into possible synthesis for commercial exploitation to ultimate destruction. Figure 1.1 from that report describes the components and their linkages. Increasingly, it is accepted that chemical discharges into sewers represent a major source of environmental contamination.

FIG. 1.1 LIFE CYCLE LINKAGES (REPRODUCED FROM ENVIRONMENT CANADA, 1986)

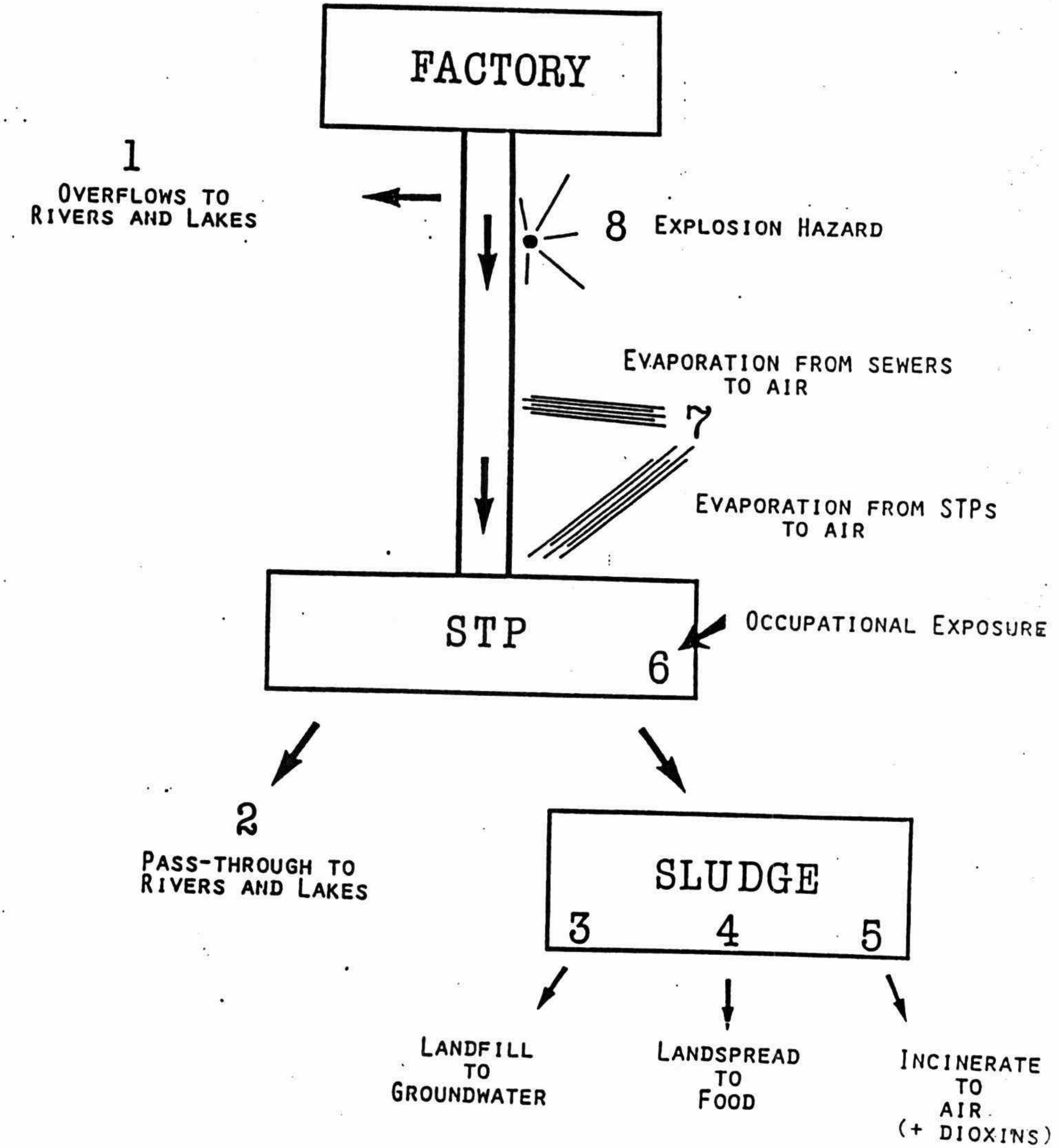


This concern has been articulated by environmental groups such as Pollution Probe in their brief "Plugging the 11,000 Loopholes in MISA" (Pollution Probe 1987), the 11,000 referring to industrial discharges to sewers. Figure 1.2 from that report shows the nature of these concerns.

Clearly there is a need to address this problem, determine its severity, and develop a capability of responding and intervening when necessary. This author believes that ultimately "decision support systems" will be in place by which rapid and sufficiently accurate assessments can be made of the fate and effects of chemicals in sewers, sewage treatment plants and the receiving environment. These systems will enable judgements of acceptable impacts on ecosystem or human health to be translated into practical control directives. Already in some jurisdictions, such as the U.S. EPA, embryonic systems of this type are in place and are scheduled for expansion and enhancement (e.g. EPA 1986).

This report addresses part of this issue, namely developing a protocol, consisting probably of calculations, computations and experimental measurements, which can be used by MOE, DOE and others, to predict the fate of hazardous contaminants in municipal sewage systems. The aim is to define the steps necessary to establish this protocol within about 2 years. The protocol should be fairly simple, scientifically sound, verified and sufficiently accurate that it will be acceptable to the Ministry, the Department, to municipalities, to industries, to environmental groups and ultimately to the concerned public.

FIG. 1.2 EIGHT THREATS TO HEALTH AND THE ENVIRONMENT WHEN INDUSTRIAL WASTES ARE SEWERED (REPRODUCED FROM POLLUTION PROBE, 1987)


FACTORY
1
OVERFLOWS TO RIVERS AND LAKES
8 EXPLOSION HAZARD
EVAPORATION FROM SEWERS TO AIR
7
EVAPORATION FROM STPs TO AIR
STP
6
OCCUPATIONAL EXPOSURE
2
PASS-THROUGH TO RIVERS AND LAKES
SLUDGE
3
4
5
LANDFILL TO GROUNDWATER
LANDSPREAD TO FOOD
INCINERATE TO AIR (+ DIOXINS)

The objectives of this study are as follows

(i) Document the present state of the art in this subject area as a result of a literature review and contributions from a meeting of experts (which was held in June 1986).

(ii) From this basis, prepare a critical and comprehensive assessment of the practicality and limitations of various approaches which may be adopted towards accomplishing the objective. Set out a tentative protocol, which it is believed, can be accomplished within 2 years.

(iii) Identify the major tasks with time and resource implications.

(iv) Prepare detailed Terms of Reference for solicitation of proposals from consultants.

This report thus consists of the following sections.

Chapter 2 - A review of the state of the art.

Chapter 3 - A discussion of various approaches leading to a tentative proposal for a protocol.

Chapter 4 - A set of Terms of Reference prepared according to prescribed guidelines, with some supporting documentation, discussion and qualifications.

It should be noted that the author of this report is entirely responsible for its content. As has been acknowledged earlier, a number of individuals contributed greatly by their comments, suggestions and corrections at the June meeting and subsequently, but ultimately the author accepts full responsibility for all statements. In assembling this document a deliberate policy was adopted of not seeking advice or information from any consultants who could potentially benefit from subsequent studies.

It is recognized that this does not present a complete account of the issue of treatability of hazardous chemicals. Such an account would be massive and probably unreadable. This report is also somewhat "distorted" in its emphasis on the research efforts with which the participants were most familiar. Other equally deserving and meritorious research programs are probably treated too lightly or even not at all.

In short, the aim is to set out what we know, what we need to know, and how we can achieve the goal of sufficient useful knowledge about the fate of hazardous contaminants in sewage treatment systems.

2. STATE OF THE ART REVIEW.

2.1 Approach.

The subject area can be conveniently divided into a number of separate issues defined by these questions.

(i) Recognizing that chemicals behave in a manner controlled by their basic molecular properties, how can reliable, relevant chemical characteristics be obtained by measurement and/or calculation? What are the relevant data? How can they be obtained? What is the role of developing structure-activity relationships? Can use be made of data bases prepared for other environmental and occupational purposes?

(ii) Can a list of perhaps 40 to 50 bench mark chemicals be established which have, or will have in the near future, well characterized properties and removability/treatability/ fate information, which can be used to help predict the fate of other chemicals believed to be somewhat similar in properties?

(iii) What studies and technology are available documenting the fate of chemicals in sewers? Are modelling/prediction schemes available?

(iv) What studies and modelling efforts have been successfully completed, or are underway, to model and predict the fate of chemicals in sewage treatment plants?

2.2 Chemical Properties.

There are over 7 million chemicals characterized in the Chemical Abstracts system. Some 50,000 are believed to be produced and used in commercial quantities and some 1000 are being introduced each year. A smaller set, variously described as a few hundred to a few thousand are considered to be of sufficient concern by virtue of the tonnage used, the nature of their use, or their high toxicity, that they have been placed on priority lists prepared by various jurisdictions. Many have been found in air, water, soils, sediments and biota, notably fish.

Some chemicals are specific, well identified molecules (e.g. benzene), others are groups of structurally related congeners (e.g. PCBs or chlorophenols), others are mixtures of numerous poorly characterized chemicals which have certain useful or desirable properties (e.g. polyelectrolytes, surfactants or aromatic solvents), and many are polymeric in nature (e.g. polyethylene). It is thus difficult to set down a meaningful list of chemicals and even more difficult to define a set of relevant properties. This issue has been addressed by various groups, for example the Ontario Ministry of Environment in its "Priority List Working Group" documents (MOE 1985), by Environment Canada and Health and Welfare Canada (Environment Canada 1986) in their deliberation about the proposed Environmental Protection Act, by OECD and EEC in various reports, by U.S. EPA as part of their administration of the Toxic Substance Control Act and Pesticides Acts. Sheehan et al. (1985) have comprehensively reviewed chemical tests from a scientific viewpoint. An examination of this literature leads to the following conclusions.

2.2.1 Organic Chemicals.

To make reliable assessments of organic chemical fate in sewage treatment systems (STSs) the following basic properties should be known.

Molecular structure and mass.

Melting point

Solubility in water.

Vapour pressure

Henry's Law Constant

Octanol-water partition coefficient (Kow)

Biodegradability (i.e. half life under defined conditions)

Sorption partition coefficients to STP biomass

Dissociation (e.g. ionization) characteristics if any.

Susceptibility to hydrolysis

Unusual properties. Examples are surface activity (e.g. foaming tendency), capacity to bind strongly to mineral or protein matter or strong odour or unusual toxicity to microbial populations.

Certain other properties may be useful, for example susceptibility to photolysis or free radical oxidation, or reactivity with chlorine or ozone, but normally such data are not as important as those mentioned above and are probably not available.

This issue of a "minimum adequate data set" has been addressed by a committee recommending changes in the Federal Environmental Contaminants Act which is to become the Environmental Protection Act (Environment Canada 1986). That group suggested three levels of data requirement with the OECD set being adopted for the most demanding level (Figure 2.1). This set coincides well with the data set suggested above, except that for STP fate assessment, more accurate and complete biodegradation data are needed. Techniques are available for calculating many of these quantities from molecular structure. Several systems are in operation which are available for purchase, an example being CHEMEST which is a computerized version of the text by Lyman et al. (1982). Some properties can be estimated from others, e.g. sorption partition coefficient from solubility or octanol-water partition coefficient, thus some economies are possible. A complication is that in some cases the values may be immeasurable, and even if they were measurable, they would not be useful. Examples are the water solubility and vapour pressure of a polymer or very high molecular weight dye. In such instances where a valid case can be made that the data are irrelevant, there is obviously little merit in demanding it.

It is believed that the properties which form an absolute minimum data set which are still capable of yielding fate and behaviour (but not toxicity) information, are:

Molecular structure and mass.

Melting Point

Solubility in water or Kow

FIG. 2.1 DATA COMPONENTS FOR THE OECD MINIMUM PRE-MARKETING SET OF DATA

Chemical identification data

Name according to agreed international nomenclature, e.g. IUPAC
Other names
Structural formula
CAS-number
Spectra ("finger-print spectra" from purified and technical grade product)
Degree of purity of technical grade product
Known impurities, and their percentage by weight
Essential (for the purposes of marketing) additives and stabilisers and their percentage by weight.

Production/Use/Disposal data

Estimated production, tons/year
Intended uses
Suggested disposal methods
Expected mode of transportation

Recommended precautions and emergency measures

Analytical methods

Physical/Chemical data

Melting point
Boiling point
Density
Vapour pressure
Water solubility
Partition coefficient
Hydrolysis*
Spectra
Adsorption - Desorption*
Dissociation constant
Particle size*

* only the screening part to be done for base set.

Acute toxicity data

Acute oral toxicity
Acute dermal toxicity
Acute inhalation toxicity
Skin irritation
Skin sensitisation
Eye irritation

Repeated dose toxicity data

14-28 days repeated dose

Mutagenicity data

Ecotoxicity data

Fish LC50 - at least 96 hours exposure

Daphnia - reproduction 14 days

Alga - growth inhibition 4 days

Degradation/Accumultion data

Biodegradation: screening phase biodegradability data (readily biodegradable).

Bioaccumulation: screening-phase bioaccumulation data (partitioning coefficient, n-octanol/water, fat solubility, water solubility, biodegradability).

Organisation for Economic Co-operation and Development, Decision of the Council (8th December, 1982) Concerning the Minimum Pre-Marketing Set of Data in the Assessment of Chemicals, C(32)196(Final).

(REPRODUCTED FROM ENVIRONMENT CANADA AND HEALTH AND WELFARE CANADA, 1986)

Vapour Pressure or boiling point (but preferably vapour pressure).

Dissociation characteristics.

Biodegradability.

Statement of any unusual properties.

A skilled analyst could probably estimate all other properties from this set with acceptable accuracy. It should be noted that the U.S. EPA new chemicals pre-manufacture notification requirements are simply molecular structure and any other available data. It is, however, acknowledged that this permits skilled analysts to conduct only an initial screening prior to acceptance or issuance of a request for more data. This is a much less rigorous scrutiny than is expected under the MISA system in which chemicals which are actually in use and being discharged will be assessed.

There is considerable and growing literature on the relationship between molecular structure, solubility, vapour pressure, Kow, sorption partition coefficients, air-water partition coefficients, dissociation constants etc. These are well reviewed in the text by Lyman et al.(1982) and in the proceedings of two symposia edited by Kaiser (1984, 1987). This subject area is advancing rapidly and it is difficult to keep abreast of all developments. This creates a problem in that most individuals in the Water Resources Branch of the Ministry are unable to devote the required time to remain cognizant of the "state of the art". Other groups in the Ministry and Department and in other agencies face similar problems and it is suggested later that a specialized central data bank and chemical property estimation system be established. This should be available to all agencies and dischargers. This would obviously benefit from liaison (and even electronic linkage) to other systems such as the U.S. EPA system in Washington or the Michigan DNR system. Access could also be made to commercial systems such as CHEMEST. The number of organic chemicals of potential interest is so large that an electronic storage and access system is indicated.

2.2.2 Metals and Inorganics.

Metals and inorganics are more limited in number, are of course non-degradable (but may be biotransformed), are usually non-volatile, and tend to have unique chemistries and biochemistries. There is a consensus that it is unlikely that structure-activity efforts which have been so successful for organics will be as successful for metals. It is recognized that in STPs, metals may undergo ionic state changes, precipitation, dissolution, chelation and conversion to organo-forms (e.g. methylation). Further, their fate is strongly dependent on conditions such as pH and temperature which prevail in the treatment process vessels.

There is considerable work underway investigating the removal of metals in STPs. A recent example is the report of Aulenbach et al. (1987) describing a mass balance for 14 metals in two stages of three plants. This study showed wide variation in performance, i.e. removal efficiency. This must reflect basic differences in chemistry. There is a belief that the removal of soluble metals by activated sludge is controlled by the complexing capacity of the sewage versus that of the sludge (Neilsen et al 1987). Neilsen et al. (1984, 1987) have shown that the removal can be related to the prevailing complexation characteristics of the system. Essentially this is the same approach as is used for organics in which sorption controls removal processes. In many cases metals exist in particulate form and are removed by physical removal processes (Neilsen & Hrudey 1983). The important point is that removal efficiencies are probably predictable given sufficient effort to understand the basic chemistry of the metal in the system. "Black-box" or empirical approaches are unlikely to lead to useful predictive capabilities.

The best approach is probably to regulate metals and inorganics on an element-specific basis, i.e. establish statements of probable mass balance in the form of amounts retained by water and sludge and use these statements to estimate loadings to receiving waters. These statements should be justifiable in fundamental chemical terms. Such statements should be based on reliable total element measurements which are fortunately relatively easy to make. The sophistication of speciation measurements in the effluent may be unnecessary because speciation is subject to later changes in the receiving environment. This large and complex issue has been reviewed recently by Bernhard et al. (1986).

Obviously, certain unusual materials such as asbestos will require custom treatment. We do not consider pathogenic or radioactive materials here since they are subject to separate control.

It is noteworthy that many of the projects supported by the Ministry's Research Advisory Committee and reported on at the Annual Technology Transfer Conference contribute information which is relevant in this context. It would be appropriate to use that effort to help fill gaps in knowledge about the properties of organic, inorganic and metallic contaminants.

2.3 Sorption.

Sorption of organics appears to be a tractable problem. Steen and Karickhoff (1981) have reviewed biosorption data for hydrophobic pollutants on a variety of natural micro-biota and obtained remarkably constant results. This indicates that the sorption process is primarily physical-chemical partitioning and characterizable using Kow or solubility. Indeed the sorption Kp is approximately 20% of Kow. Somewhat similar results were obtained by Blackburn et al.(1985). There is a considerable and growing literature on sorption and biosorption which we make no attempt to review here. A high degree of predictability is often obtained.

To illustrate this we can assemble a simple mass balance. If in Vm^3 of liquid there is vm^3 of biomass, the total concentration of chemical is C_T, the dissolved concentration is C_W and the sorbed concentration is C_S then

$$VC_T = v^{C}{}_S + (V-v)C_W$$

But the sorbed and dissolved concentrations are related by a partition coefficient K_P

$$\text{i.e. } C_S = C_W K_P$$

$$\text{thus } VC_T = C_W(vK_P + V-v)$$

Usually v is negligible compared to V thus

$$C_W/C_T = 1/(1 + vK_P/V) = 1/(1 + C_B K_P)$$

i.e. this is the fraction in solution. The key group is thus vK_P/V, or the product of K_P and the biomass concentration (in volume fraction units) C_B or v/V. If $C_B K_P$ is unity there is equipartitioning. If it exceeds, one sorption dominates and vice versa. C_B is usually known, thus even an approximate value for K_P, as obtained from K_{OW}, is often sufficient to define the system adequately.

It thus appears that it will be possible to relate extent of sorption to biomass to variables such as MLSS or VSS using Kow to quantify hydrophobicity. Some experimental verification under typical STP operating conditions is desirable.

2.4 Volatility.

Volatilization or stripping also appears to be a tractable problem since it is almost entirely a physical process, although it is modified by sorption and by the rate of biodegradation. The key variable is the Henry's Law constant which can be calculated from solubility and vapor pressure, or measured directly. Roberts et al.(1983, 1984) have examined this issue in some detail and have shown that the systems behave in a generally predictable manner. Truong and Blackburn (1984) have described experiments and a model for organic chemical stripping from pilot scale STPs. Lurker et al. (1982) have measured emissions of organo-chlorine chemicals from the Memphis Tenn. STP and have shown appreciable emissions from the aeration process or in some cases from the grit chamber.

It should thus be possible to model this process with acceptable accuracy and apply these models to all vessels in the STP. The approaches used by Roberts et al. (1983, 1984) and Blackburn et al. (1985) are soundly based in physical chemical principles and are the obvious modelling starting point. The key issues are determination of extent of chemical availability to volatilization as controlled by sorption and the extent of exposure to air as controlled by area - mass transfer coefficient products or aeration rates.

2.5 Biodegradability.

2.5.1 The Options for Treatability Assessment.

Biodegradability assessment has been the subject of numerous studies, most experimental, but more recently computational in nature. At the June meeting this topic was discussed exhaustively. The consensus reached was that there are still difficulties with all approaches used to assess biodegradability, and no one approach has yet emerged as universally favoured. In this situation the best strategy is probably to maintain all options and devote continuing research effort to enhancing their reliability. Eventually a consensus may develop on a "standard" approach.

Grady (1980) has recently compiled a comprehensive review of hazardous waste biodegradation in conventional treatment plants with 210 references. This is an available source of information and includes research suggestions.

The options or approaches are:

(1) The use of structure-activity relationships involving computation of molecular properties or consideration of chemical groups present to correlate and predict biodegradability.

(2) The use of simple litre scale, usually batch, but sometimes sequential, laboratory tests in which the loss of chemical by biodegradation is measured experimentally.

(3) The use of pilot scale tests, usually operated continuously which attempt to mimic full scale treatment systems.

(4) The acquisition of performance/fate data from operating STPs.

Each option has advantages and disadvantages in terms of cost, repeatibility, reliability, time necessary, availability of data etc. We discuss each option in turn below.

2.5.2 Structure-Activity Relationships (SAR).

At the June meeting Dr. Dearden of the University of Liverpool reviewed the history of biodegradability SARs. A number of workers including Enslein, Veith, Paris, Boethling, Howard, Banerjee, Mudder, and Pitter have addressed aspects of the issue and some success has been achieved in relating biodegradability to structure. A basic problem, highlighted by Dr. Howard is that there is still no published, peer reviewed, validated set of "reliable" biodegradability data which can be used as a foundation for SAR development. The data set which comes closest to the ideal is that for 5 day BOD data for 240 chemicals which has been intensively screened for the EPA Environmental Research Laboratory at Duluth, but it has not been formally published. It is, however, widely available. Howard et al (1987) have also addressed this issue and categorized chemicals as shown in Tables 2.1 to 2.4.

Dr. Boethling described the U.S. EPA approach which is essentially informed judgement by a skilled analyst. He has recently (Boethling 1986b) reviewed the application of molecular topology indices (e.g. connectivity) as descriptors of molecular shape, (especially branching) which influence biodegradability. This approach is promising but also lacks a sound mechanistic base.

The molecular descriptors used have included Kow, solubility, connectivity, molar volume, parachor, total surface area, atomic charges and differences. The most successful effort has been by Dearden who has used available molecular computational programs (CNDO2 and Molecular Mechanics) to calculate a charge difference term D between the atoms which are believed to be the point of initial enzymatic attack. This approach has been remarkably successful, a linear correlation existing between percent BOD (as reported in the EPA data set) and the term D. The correlation has successfully confirmed the point of attack in multifunctional molecules. It is being tested by being operated in a predictive mode, i.e. estimating percent

TABLE 2.1 BIODEGRADABILITY AND RELIABILITY CODES FOR ORGANIC COMPOUNDS (REPRODUCED FROM HOWARD ET AL, 1987)

Biodegradability code	Description
BF	Biodegrades at a Fast rate
BFA	Biodegrades at a Fast rate with Acclimation
BS	Biodegrades at a Slow rate
BSA	Biodegrades at a Slow rate even with Acclimation
BST	Biodegrades Sometimes
NB	No Biodegradation
NE	No Evaluation
1	Chemical tested in three or more tests, consistent results
2	Chemical tested in two tests or results in more than two tests are interpretable but some conflicting data
3	Only one test or uninterpretable conflicting data

TABLE 2.2 FORMAT FOR A SUMMARY RECORD IN BIODEG AND AN EXAMPLE RECORD (REPRODUCED FROM HOWARD ET AL, 1987)

(PAR)	Parameter Type	BIODEGR: SUMMARY
(CAS)	CAS Registry No.	75-65-0
(NAM)	Chemical Name	t-Butanol
(REC)	Record Number	3
(STS)	Aerobic Screening Test—Summary	BST
(STR)	Aerobic Screening Test Reliability	1
(BTS)	Aerobic Biological Treatment Simulation—Summary	BST
(BTR)	Aerobic Biological Treatment Simulation—Reliability	1
(GSS)	Aerobic Grab Sample—Summary	BS
(GSK)	Aerobic Grab Sample—Reliability	2
(FTS)	Aerobic Field Test—Summary	
(FTR)	Aerobic Field Test—Reliability	
(ABS)	Aerobic Biodegradation—Summary	BST
(ABR)	Aerobic Biodegradation—Reliability	1
(AWS)	Anaerobic—Water—Summary	
(AWR)	Anaerobic—Water—Reliability	
(ASS)	Anaerobic—Soil—Summary	
(ASR)	Anaerobic—Soil—Reliability	
(ANS)	Anaerobic Biodegradation—Summary	
(ANR)	Anaerobic Biodegradation—Reliability	
(PCS)	Pure Culture	
(NRU)	Number of References Used	15
(DTE)	Date Evaluated	8-15-84

TABLE 2.3 Criteria for determining whether biodegradation is "fast" or "slow" in screening tests

Test	Slow	Fast	Units
MITI	0–29	30–100	% BODT in 14 d
MITI	0–59	60–100	% BODT in 28 d
Pitter	0–89	90–100	% COD in 5 d
OECD-Coupled Units	0–19	20–100	% degradation (specific analysis)
	0–69	70–100	% mineralization (CO_2)
AFNOR	0–59	60–100	% DOC disappearance in 28 d
AFNOR	0–69	70–100	% DOC disappearance in 28 d
Sturm	0–49	50–100	% theoretical CO_2 in 28 d
Sturm	0–59	60–100	% theoretical CO_2 in 28 d
OECD-Screening	0–59	60–100	% DOC disappearance in 28 d
OECD-Screening	0–69	70–100	% DOC disappearance in 28 d
OECD-Screening	0–69	70–100	% DOC disappearance in 28 d
Closed-Bottle	0–49	50–100	% BODT in 28 d
Closed-Bottle	0–59	60–100	% BODT in 28 d
Closed-Bottle	0–59	60–100	% BODT in 28 d
EMPA	0–39	80–100 (uncertain 40–79)	% DOC disappearance in 14 d

(REPRODUCED FROM HOWARD ET AL, 1987)

TABLE 2.4 Sample of biodegradation evaluation for 1,2-diaminoethane

Reference	Method	Incubation time (d)	Chem. conc. (ppm)	Acclimation period (d)	Rate	Rate units	Study biodegradation code	Summary biodegradation – reliability codes
[34]	BOD	10		28[a]	80	% BODT	BFA	
[13]	COD							
	Removal	5	200(C)[b]	20	97.5	% COD Removal	BFA	
[26]	Salt-water	5	3–10		2	% BODT	BS	
	BOD	10	3–10		14	% BODT		
		15	3–10		16	% BODT		
		20	3–10		16	% BODT		
[26]	BOD	5	3–10	0	24	% BODT	BF	
		10	3–10	0	44	% BODT		
		15	3–10	0	55	% BODT		
		20	3–10	0	47	% BODT		
		5	3–10	45–60	36	% BODT	BFA	
		10	3–10	45–60	45	% BODT		
		15	3–10	45–60	56	% BODT		
		20	3–10	45–60	70	% BODT		
[35]	Sea-water	5	7–10		16.6	% BODT	BS	
	BOD							
	BOD	5	7–10		0.55	% BODT	BS	
								Aerobic Screening Tests BFA-1
[27]	Field study	0	40		40	Residue	NE[c]	
	drainage	1			10	conc.		
	ditch	7			0	remaining		
		14			0	(ppm)		
		21			0			
	Field study	0	40		40	Residue	NE[c]	
	applied to	1			22	conc.		
	soil surface	6			15	remaining		
	of tomato	13			20	(ppm)		
	plant bed	27			0			
								Summary aerobic biodegradation BFA-1

[a] 10-d acclimation of river water sample to diethanolamine and then 28-d acclimation period to 1,2-diaminoethane.

[b] ppm of carbon as test chemical.

[c] Deionized water used as a control-residue concentration remaining (ppm) 100, 45, 40, 40, trace at days 0, 1, 7, 14, 21, respectively; no evaluation because of loss in controls.

(REPRODUCED FROM HOWARD ET AL, 1987)

BOD for molecules for which no BOD data are available, with complementary BOD measurements being made at the Water Research Centre in the U.K.

The problem is that no one (including Dearden) understands the mechanistic basis of the SAR. It is conceivable, (but unlikely), that agreement is merely fortuitous. The consensus emerged at the June meeting, and at the 2nd. QSAR Workshop (which was held the previous week at McMaster University and organized by Dr. Klaus Kaiser) that the approach is excellent, promising and should be pursued vigorously, but that it is premature to use it in a predictive mode until it is better validated and some explanation can be found for its mechanism.

Another concern is that it is well known that lipophilicity, (e.g. Kow) influences biodegradability because it controls water-organism partitioning. But this factor does not enter the BOD assessment process. Probably the most comprehensive account of the basis and use of hydrophobic descriptors such as Kow and solubility is given in the review by Dearden (1985). Although this work has primarily focussed on predicting the effects of drugs and toxic chemicals it is relevant to the issue of sorption of organics to biomass and probably also to biodegradation kinetics.

Pitter (1976, 1985a, 1985b) has reported and interpreted experimental biodegradability data for a considerable number of organic chemicals, Mudder (1981) has also analysed these data and has established predictive systems, but not of generally acceptable accuracy.

Dr. Howard described ongoing work at Syracuse Research Corp in which biodegradability categories are being developed (described earlier) which would be suitable for use in Chemical Information Systems. The codes not only include those describing degradability but also descriptions of reliability which is a judgement assigned by the assessor based on the amount of, and agreement between, available experimental data. In many cases no evaluation is possible. An attractive feature of this system is that it certainly can be implemented. i.e. it can be regarded as a totally feasible "fallback" system if all else fails.

An interesting ongoing experiment in biodegradability assessment was described by Dr. Boethling in which 25 to 30 experts in biodegradability are being presented with a list of chemicals and are being asked to express an expert judgement (without experiment) of biodegradability. The results of this trial will be interesting in that they may shed light on the issue of how successful expert judgement can be in predicting biodegradability. It is conceivable that intuitive reasoning based on experience is more accurate than has been appreciated by scientists who tend to have an inbred scepticism. If experts are successful, an implication follows that computer systems based on knowledge-based, expert or artificial-intelligence systems could eventually play a role in assessing biodegradability. Such efforts could be enhanced by SAR computations. EPA is sponsoring some work in this area, but it is too early to comment on its success. Unfortunately success is unlikely within 2 years.

An example of this type of approach is a recent paper by Niemi et al. (1987) which examines the chemical structural features associated with degradation of 287 chemicals in the "EPA data set". Certain structures such as the presence of one tert-butyl terminal branch or a cyano group or more than one amino group on a ring with nitrogen a member of the ring, seem to impart recalcitrance.

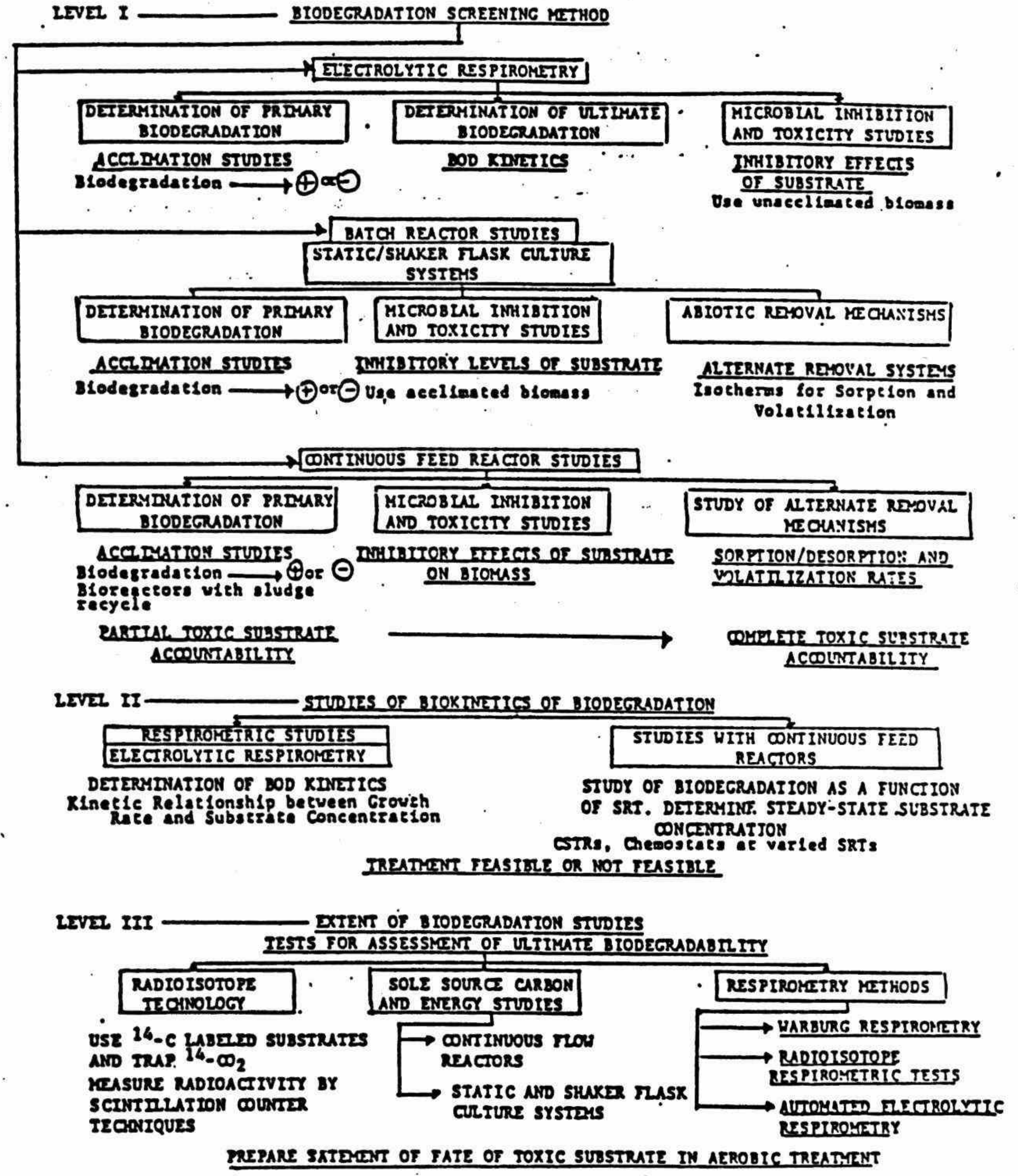
2.5.3 Bench Scale Systems.

A number of bench scale systems have been devised, for example BOD tests, shake flask, OECD tests. Boethling (1986a) has recently reviewed laboratory methods of environmental biodegradation assessment and has stressed the need for validation and field testing with a wider variety of chemicals. These tests are relatively fast and inexpensive and can be used to generate data to "categorize" chemicals. In the view of many workers, the most advanced efforts of this type are those at the U.S. EPA Laboratory at Cincinnati described by Tabak, Bishop, Hannah and others. This group, most notably Tabak, has examined and devised several systems for aerobic and anaerobic testing involving shake flask, continuous feed and sequential contacting batch systems. Tables 2.5 and 2.6 give flowcharts of the logic diagram for the aerobic and anaerobic systems (kindly provided by Dr. Hannah) and described in the multi-level comprehensive aerobic and anaerobic biodegradation testing protocol developed by Tabak (1986) which is designed to determine the biodegradability, provide kinetic parameters and measure the

TABLE 2.5 LOGIC FLOW DIAGRAM FOR THE BIODEGRADATION TESTING PROCEDURE

AEROBIC SYSTEMS

AEROBIC BIODEGRADATION TESTING

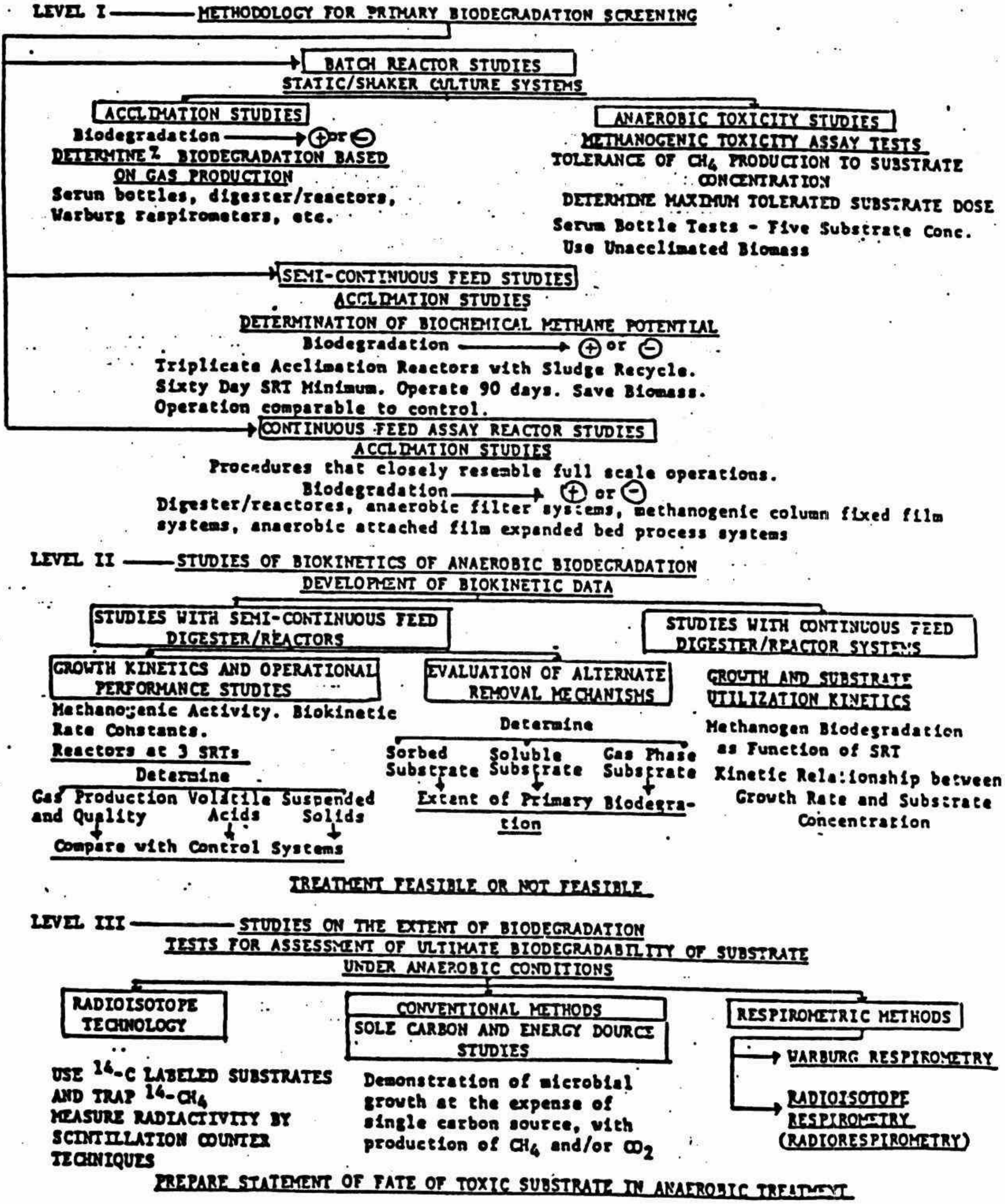

LEVEL I
BIODEGRADATION SCREENING METHOD
ELECTROLYTIC RESPIROMETRY
DETERMINATION OF PRIMARY BIODEGRADATION
DETERMINATION OF ULTIMATE BIODEGRADATION
MICROBIAL INHIBITION AND TOXICITY STUDIES
ACCLIMATION STUDIES
Biodegradation → ⊕ or ⊖
BOD KINETICS
INHIBITORY EFFECTS OF SUBSTRATE
Use unacclimated biomass
BATCH REACTOR STUDIES
STATIC/SHAKER FLASK CULTURE SYSTEMS
DETERMINATION OF PRIMARY BIODEGRADATION
MICROBIAL INHIBITION AND TOXICITY STUDIES
ABIOTIC REMOVAL MECHANISMS
ACCLIMATION STUDIES
Biodegradation → ⊕ or ⊖
INHIBITORY LEVELS OF SUBSTRATE
Use acclimated biomass
ALTERNATE REMOVAL SYSTEMS
Isotherms for Sorption and Volatilization
CONTINUOUS FEED REACTOR STUDIES
DETERMINATION OF PRIMARY BIODEGRADATION
MICROBIAL INHIBITION AND TOXICITY STUDIES
STUDY OF ALTERNATE REMOVAL MECHANISMS
ACCLIMATION STUDIES
Biodegradation → ⊕ or ⊖
Bioreactors with sludge recycle
INHIBITORY EFFECTS OF SUBSTRATE ON BIOMASS
SORPTION/DESORPTION AND VOLATILIZATION RATES
PARTIAL TOXIC SUBSTRATE ACCOUNTABILITY
COMPLETE TOXIC SUBSTRATE ACCOUNTABILITY
LEVEL II
STUDIES OF BIOKINETICS OF BIODEGRADATION
RESPIROMETRIC STUDIES
ELECTROLYTIC RESPIROMETRY
STUDIES WITH CONTINUOUS FEED REACTORS
DETERMINATION OF BOD KINETICS
Kinetic Relationship between Growth Rate and Substrate Concentration
STUDY OF BIODEGRADATION AS A FUNCTION OF SRT. DETERMINE STEADY-STATE SUBSTRATE CONCENTRATION
CSTRs, Chemostats at varied SRTs
TREATMENT FEASIBLE OR NOT FEASIBLE
LEVEL III
EXTENT OF BIODEGRADATION STUDIES
TESTS FOR ASSESSMENT OF ULTIMATE BIODEGRADABILITY
RADIOISOTOPE TECHNOLOGY
SOLE SOURCE CARBON AND ENERGY STUDIES
RESPIROMETRY METHODS
USE 14-C LABELED SUBSTRATES AND TRAP 14-CO2
MEASURE RADIOACTIVITY BY SCINTILLATION COUNTER TECHNIQUES
CONTINUOUS FLOW REACTORS
STATIC AND SHAKER FLASK CULTURE SYSTEMS
WARBURG RESPIROMETRY
RADIOISOTOPE RESPIROMETRIC TESTS
AUTOMATED ELECTROLYTIC RESPIROMETRY
PREPARE SATEMENT OF FATE OF TOXIC SUBSTRATE IN AEROBIC TREATMENT

reproduced from Tabak, H.H. (1986) "Protocol for Determining Biodegradation of Organic Toxic Pollutant Compounds in Aerobic and Anaerobic Wastewater Treatment Systems"

TABLE 2.6 LOGIC FLOW DIAGRAM FOR THE BIODEGRADATION TESTING PROCEDURES

ANAEROBIC SYSTEMS

ANAEROBIC BIODEGRADATION TESTING


LEVEL I — METHODOLOGY FOR PRIMARY BIODEGRADATION SCREENING
BATCH REACTOR STUDIES
STATIC/SHAKER CULTURE SYSTEMS
ACCLIMATION STUDIES
Biodegradation → ⊕ or ⊖
DETERMINE % BIODEGRADATION BASED ON GAS PRODUCTION
Serum bottles, digester/reactors, Warburg respirometers, etc.
ANAEROBIC TOXICITY STUDIES
METHANOGENIC TOXICITY ASSAY TESTS
TOLERANCE OF CH_4 PRODUCTION TO SUBSTRATE CONCENTRATION
DETERMINE MAXIMUM TOLERATED SUBSTRATE DOSE
Serum Bottle Tests - Five Substrate Conc.
Use Unacclimated Biomass
SEMI-CONTINUOUS FEED STUDIES
ACCLIMATION STUDIES
DETERMINATION OF BIOCHEMICAL METHANE POTENTIAL
Biodegradation → ⊕ or ⊖
Triplicate Acclimation Reactors with Sludge Recycle.
Sixty Day SRT Minimum. Operate 90 days. Save Biomass.
Operation comparable to control.
CONTINUOUS FEED ASSAY REACTOR STUDIES
ACCLIMATION STUDIES
Procedures that closely resemble full scale operations.
Biodegradation → ⊕ or ⊖
Digester/reactores, anaerobic filter systems, methanogenic column fixed film systems, anaerobic attached film expanded bed process systems
LEVEL II — STUDIES OF BIOKINETICS OF ANAEROBIC BIODEGRADATION
DEVELOPMENT OF BIOKINETIC DATA
STUDIES WITH SEMI-CONTINUOUS FEED DIGESTER/REACTORS
STUDIES WITH CONTINUOUS FEED DIGESTER/REACTOR SYSTEMS
GROWTH KINETICS AND OPERATIONAL PERFORMANCE STUDIES
Methanogenic Activity. Biokinetic Rate Constants.
Reactors at 3 SRTs
Determine
Gas Production and Quality
Volatile Acids
Suspended Solids
Compare with Control Systems
EVALUATION OF ALTERNATE REMOVAL MECHANISMS
Determine
Sorbed Substrate
Soluble Substrate
Gas Phase Substrate
Extent of Primary Biodegration
GROWTH AND SUBSTRATE UTILIZATION KINETICS
Methanogen Biodegradation as Function of SRT
Kinetic Relationship between Growth Rate and Substrate Concentration
TREATMENT FEASIBLE OR NOT FEASIBLE
LEVEL III — STUDIES ON THE EXTENT OF BIODEGRADATION
TESTS FOR ASSESSMENT OF ULTIMATE BIODEGRADABILITY OF SUBSTRATE UNDER ANAEROBIC CONDITIONS
RADIOISOTOPE TECHNOLOGY
USE ^{14}-C LABELED SUBSTRATES AND TRAP ^{14}-CH_4
MEASURE RADIACTIVITY BY SCINTILLATION COUNTER TECHNIQUES
CONVENTIONAL METHODS
SOLE CARBON AND ENERGY DOURCE STUDIES
Demonstration of microbial growth at the expense of single carbon source, with production of CH_4 and/or CO_2
RESPIROMETRIC METHODS
WARBURG RESPIROMETRY
RADIOISOTOPE RESPIROMETRY (RADIORESPIROMETRY)
PREPARE STATEMENT OF FATE OF TOXIC SUBSTRATE IN ANAEROBIC TREATMENT

reproduced from Tabak, H.H. (1986) "Protocol for Determining Biodegradation of Organic Toxic Pollutant Compounds in Aerobic and Anaerobic Wastewater Treatment Systems" extent of biodegradation of toxic organic compounds by the microbial consortia of aerobic and anaerobic waste treatment systems. It is clear that in any attempt by MOE or DOE to devise a system for Ontario, close liaison should be maintained with Tabak and his colleagues because of their unique experience.

Howard and Banerjee (1984) have reviewed biodegradability testing and have identified research needs, notably the need for better screening tests, the use of benchmark chemicals, more field studies (which in this case could be viewed as STP studies). Suggatt et al.(1984) as part of the Syracuse Research Corp. experimental program studied the shake flask biodegradation of 14 phthalate esters. This work is of interest in that the phthalate esters are frequently regarded as persistent, yet they degraded appreciably. There are also useful insights into the test protocol which differentiates between loss of parent chemical and ultimate degradation as measured by CO2 evolution. An EPA report by Tabak et al. (1981) describes determination of the biodegradability of all the EPA Priority pollutants using a static flask system suitably modified to allow for variations in volatility and solubility. Data are given for extent of biodegradability and acclimation for 96 chemicals. Kirsch et al. (1986) and Kirsch and Wukasch (1986) in association with EPA have developed a protocol for predicting the fate of organics in STPs. The testing involves studies of aerobic acclimation, biokinetics, extent of degradation and anaerobic testing. Rochkind et al. (1986) have reviewed the factors influencing the biodegradation of chlorinated aromatics, which are generally perceived to be among the most poorly degraded chemicals and thus of primary concern to the MISA program. They stress the need for acquisition of all relevant data in STPs and not merely removal. Urano and Kato (1986a,b) of Yokohama National University have described a test method (an electrolytic respirometer), its use on 11 chemicals and development of 4 indices: -a lag time, a rate constant, a degradation time, and the percent BOD removal. Chemicals were then assigned to one of 10 groups representing the completeness, time and acclimation properties. The groups are more detailed than the Howard-Boethling system. Tabak and Grady (1988) have developed a protocol to determine biodegradability and biodegradation kinetics of toxic organic compounds from respirometric data using electrolytic respirometry.

The EEC in its Directive 79/83, Annex V Part C "Methods for the Determination of Ecotoxicity, 5.2 Degradation, Biotic Degradation" specifies the OECD test, the AFNOR T 90-302 test, the Sturm test, the MITI test and closed bottle test. An account of test reproducibility has been given by Richterich and Gerike (1986). Patterson and Kodukala (1981) have reviewed and presented results of biodegradation rate studies of the EPA priority list.

It is likely that the Ministry and/or the Department will find it necessary to set up and operate, on request, a bench scale system of this type which can be used to obtain experimental data in support of treatability assessments. We return to this issue later when proposing a method of determining which system or systems are best suited for this purpose.

An important and enlightening perspective was provided at the June meeting by Dr. Blackburn from the University of Tennessee who discussed the marked differences in biodegradability assessments resulting from the various approaches. Pure culture studies are essentially a test of the genetic capability of an organism to degrade the chemical as influenced by cellular physiology. Bench, pilot and full scale systems are also influenced by factors such as residence time distribution, hydrodynamics, aeration and stripping. Ecological systems are also influenced by population dynamics, trophic level interactions, competition between dynamically varying populations and the availability and cycling of energy and nutrients. It is thus clear that it is naive to assign each molecule a property termed average "biodegradability" (as can be done with molecular weight) because it is not only a property of the molecule but also of the biological environment which it experiences. That environment is influenced by other factors many including the breakdown of other chemicals which are present. However, for practical purposes some method must be found to assign numerical biodegradability characteristics to a molecule which reflect its treatability in STPs.

Finally there are two worrisome problems.

Biotransformation of a molecule is not a single stage process. Disappearance of the original molecule should not be confused with mineralization to CO2 and water. Identifying metabolites and deciding if these metabolites are more or less persistent or hazardous than the parent molecule is difficult and is a problem which must probably be treated as secondary in this context in the next few years. Second, as Dr. Melcer pointed out there may be considerable discrepancies between bench scale degradation rates and those observed in pilot or full scale tests. The example of dinitrocresol was cited. It must be appreciated that the state of the art is such that assessments can only be made with the "best available techniques" and there will be inadequacies.

2.5.4 Pilot Scale Systems.

At the June meeting a number of pilot scale continuous systems were described including the efforts at Oklahoma State University by Dr. Stover in association with Dr. Kincannon, at the Wastewater Technology Centre at Burlington by Dr. Melcer, at Tennessee by Dr. Blackburn, at U.S. EPA Cincinnati by Dr. Hannah. Note was also taken of the efforts at Purdue University (Wukasch), at Clemson (Grady), at Michigan (Weber) and at Stanford (Roberts).

Stover and Kincannon (1983) described the treatability of 12 chemicals in a 6.23 litre total capacity activated sludge system and obtained data on stripping and biodegradation. This lab system involves cell residence times of from 2 to 6 days and was operated for 60 day periods. Stover (1985) has recently reviewed the removal of organics in STPs with special emphasis on chlorinated compounds. Comparison was made with static screening results. A related report from the same group treats the issue of design guidelines for STPs handling such chemicals in petroleum refinery effluents (Stover, Gomathinayogan and Gonzales (1985). Stover, Fazal and Kincannon (1986) have examined the feasibility of "assisting" the removal of organics by the use of ozone and activated carbon at a STP. Kincannon et al. (1983) also studied 15 organic chemicals in a pilot STP and investigated the use of ozone. Petrasek et al. (1983) reported the results of a pilot activated sludge plant spiked with 22 chemicals (4 pesticides, 3 phenols, 6 phthalates and 9 PAHS). Mass balances were established not only for influent and effluents but also in the return sludge and the effluent air.

These systems are invaluable as a means of obtaining scientific information about treatability, about relative fate by degradation, volatilization and sorption to sludge, for assisting in formulating and calibrating models. They are probably not feasible for routine use for assessment of individual chemicals - except in unusual circumstances.

2.5.5 Full Scale Systems.

A number of reports have been issued on treatability in fullscale systems. Most of these have been reviewed by Melcer (1986). Convery et al. (1980) have desribed the occurrence of EPA priority pollutants in 25 STPs and have provided a comprehensive account of the regulatory and analytical context. Several EPA Contract reports have documented chemicals in effluents from industrial and municipal systems. Results from such programs have been reported or discussed by Engineering Science Inc. (1982), Cantest and IEC for PACE (1981), Burns and

Roe (1979, 1980, 1982), Jordan (1982), Cohen et al. (1981), Hannah (1982), Canviro (1984), Oliver and Cosgrove (1975).

These data can not generally be used to assess degradability for several reasons.

Measurement of only input and output in water (as is usual) includes other removal processes notably sorption and volatilization. There may also be considerable temporal variability in inlet outlet and recycle stream concentrations, thus it is not easy to state that a chemical in a "package" of inlet water experienced a certain fate. Many "exotic" chemicals are discharged as pulses to STSs, not as regular emissions. Spot sampling can thus be highly misleading.

At the June meeting, Dr. Melcer described a current project being conducted by Environment Canada examining time variations of influent and effluent concentrations of selected chemicals. A paper placing this work in perspective with previous studies was later published in the MOE Technology Transfer Conference Proceedings (Melcer 1986). A valuable feature of this review is the documentation of the chemicals most fequently encountered in STP influents and effluents.

A consensus emerged that since the ultimate aim is to predict the performance of full scale systems, and doubts will always exist about our ability to extrapolate from small to large scale, there is a need to gather and analyse full scale system performance. Because full scale studies are so difficult and expensive, one attractive strategy would be to identify for study a number of "bench mark" chemicals which have the following characteristics:

(a) well established properties.

(b) easy and inexpensive to analyse by well established protocols.

(c) present in many effluents at fairly constant and substantial concentrations.

(d) have been subjected to thorough bench and pilot scale testing.

(e) represent, in total, a spectrum of fate processes, i.e. include a range of biodegradability, volatility, and sorptive properties.

(f) ecotoxicologically significant in most cases.

These chemicals could be tested for in various municipal STPs to gain information on relative performance under various operating characteristics and to help validate models which may be used as part of the MISA program.

A relatively simple method of assessing the fate of a new chemical would then be to seek the bench mark chemical which it most closely resembles. This technique has been successfully devised by Gillett (1986) at Cornell University for environmental fate assessment as the BIOS system.

Following Melcer (1986) the most promising candidate chemicals are

Volatiles:- chloroform, methylene chloride, tetrachloroethylene, benzene, toluene, 1,1,1-trichloroethane, xylenes, trichloroethylene and ethylbenzene

Base Neutrals:- naphthalenes, various phthalate esters, chlorobenzenes

Acids:- phenol, cresols

Metals:- cadmium, chromium, copper, lead, nickel, zinc, arsenic, silver, antimony

Inorganics:- cyanide

It is recognized that this list contains some "overlapping" chemicals, i.e. with similar properties, but this is useful to confirm predictability. The list also lacks representation from several important classes such as phenoxy-acid herbicides, chloro-phenols, surfactants and heterocycles. But it is a starting point from which valuable data can be obtained.

Recently the Ministry has produced a list of Effluent Monitoring Priority Chemicals (Ministry of Environment 1987). This provides a comprehensive discussion and listing of chemicals which are candidates.

2.6 Fate in Sewers.

A search was made of the literature, but little information was obtained. A number of studies are being made to measure concentrations of chemicals in off or vent gases and in the vicinity of waste waters largely for occupational purposes. The U.S. EPA is currently studying this issue in its Cincinnati Laboratory under the direction of Dr. F. Bishop. Very little has been published.

It is believed that the extent of biodegradation in the sewer system will, in most cases, be small compared to the STP.

In those cases where appreciable biodegradation does occur in sewers, it is likely that almost complete degradation occurs in the STP. An argument can thus be made, albeit weakly, that there is little merit in assessing biodegradability in the sewer system except for very degradable, volatile chemicals.

Volatilization is likely to be much more important, but from a different perspective. If appreciable sewer volatilization occurs, then even greater STP volatilization is expected because of the deliberately enhanced air-water contacting. But volatile emissions into sewers and thence through manholes and other vents to the atmosphere may cause public health and nuisance concerns. There are frequent public complaints about smells from sewers. This volatilization may be enhanced by hydraulic jumps, deep drops, pumping and other hydraulic activities.

It is believed that a capability is needed within the Ministry as part of the MISA program to compute or estimate volatile chemical emissions from sewers as a function of amounts discharged. It is expected that in many cases the results will indicate that certain chemicals should not be discharged to sewers because this is essentially equivalent to allowing them to evaporate from a pool outdoors. Recycle, avoidance or special treatment are obviously preferable. This calculation of volatilization must obviously take into account sorption, largely to organic matter. This is not expected to be a difficult problem.

It is recommended that when findings from the current EPA work are available, a research program be mounted to translate these findings to the Ontario scene and to develop a predictive capability suitable for use in estimating the extents of volatilization and degradation.

2.7 Fate in Sewage Treatment Plants

2.7.1 Predictive Models

A considerable number of studies have been made of chemical fate in STPs and several modelling attempts have been made and reported. At the June meeting a number of models were described including the Blackburn et al. (1983) model, the Stover-Kincannon model (Stover and Kincannon 1983), the Mackay-Henry-Clark Fugacity model (Clark et al. 1986), the Weber-Jones model (Weber and Jones 1980), and mention was made of other efforts including those of Roberts et al. (1983, 1984), and Wukasch, Grady and Kirsch (1981). Many models are in various developmental stages and are not fully published or documented.

A consensus was reached that none of the existing models is adequate for use in an abatement system such as MISA but an achievable goal would be the establishment of such a model within 2 years. Some of the features of the models are reviewed briefly below.

Stover - Kincannon Model.

The authors start from the premise that the kinetic design and performance evaluation of the activated sludge process is best described using the well established biokinetic predictive models developed by Gaudy, Lawrence, McCarty and Eckenfelder.

These equations, however, assume the substrate is removed only by biological action. The model devised by Stover and Kincannon uses a similar approach in applying these equations, with modifications to the mass balance to include stripping and adsorption, as well as biological conversion. They proposed that the biological kinetic coefficients should be developed after first subtracting the equivalent amount of BOD, TOC or COD lost through other mechanisms.

Blackburn Model.

An overall mathematical predictive fate model was developed by Blackburn et al. (1983) to predict the equilibrium aqueous phase concentration of organics in the secondary effluent from an activated sludge plant. A stripping predictive fate model and an equilibrium adsorptive predictive fate model are incorporated into traditional design models used in environmental engineering.

The stripping predictive fate model estimates the rate of air stripping of the chemical, with the stripping rate constant determined empirically to be related to the Henry's Law Constant, the air flowrate and the reactor volume. The adsorption predictive model proposes an equation relating the octanol-water partition coefficient and the equivalent lipid fraction in the biomass to the aqueous-biomass distribution coefficient. This equation is based upon the theory, discussed earlier, that adsorption occurs into the internal lipids of the biomass. The bio-oxidation or degradation process was assumed to follow a first-order reaction rate with a rate constant either fitted from experimental data or estimated by other methods.

Fugacity Model.

A predictive model based on the fugacity modeling system has been proposed by Clark et al. (1986). Fugacity is a thermodynamic concept which can be thought of as the "escaping tendency" of a chemical from the phase in which it is present to another phase. Fugacity (units of pressure) is related linearly to concentration. Fugacity capacity coefficients, which are a measure of the ability of the phase to "soak up" the component of concern, are determined for air, water and biomass. By estimating the prevailing fugacity in the primary, aeration and secondary settling tanks, the chemical concentration in the water, air and sludge can be calculated.

The concentration of the chemical in the air is estimated using the Henry's Law Constant and the truly dissolved chemical concentration, while the concentration adsorbed onto the sludge is determined using the partition coefficient, using a similar approach to Blackburn et al. (1983). The equations developed using the fugacity approach finally resemble algebraically those obtained empirically by Blackburn et al. (1983). Biodegradation is estimated assuming a first-order rate of reaction. This is, of course a weakness in this and similar models, but if information was available to characterize non-first-order kinetics it could be incorporated.

Roberts Model.

The model proposed by Roberts et al. (1984) estimates the removal of volatile organic solutes from aeration tanks in a wastewater treatment plant. This model is more rigorous than those discussed above, and is based on the oxygen transfer coefficient as a means to characterize the extent of approach to equilibrium between air and water. The method consists of comparing liquid-phase transfer rate constants of individual compounds with that of oxygen to obtain a proportionality factor.

Grady - Wukasch - Kirsch Model.

The model by Grady, Wukasch and Kirsch attempts to predict kinetic relationships and effluent quality stated as a function of the solids retention time and the specific growth rate of the microorganisms. The amount of degradation is estimated using a first order function based on the specific growth rate.

Stripping and adsorption are estimated by applying factors determined experimentally to full scale plant data. The contribution of adsorption is estimated by multiplying the quantity of waste sludge produced daily by the experimentally determined adsorptive capacity. The contribution of stripping is predicted using a ratio based on the reactor conditions and flow rates. It is assumed that the ratio of mass transfer coefficients of the substrate in the test and full-scale is equal to the ratio of the coefficients for oxygen transfer in the same reactors.

Conclusions.

The models are believed to provide a good description of the processes of transport, sorption, and volatilization. The principal weakness lies in their treatment of biodegradation kinetics. This is a complex process which remains poorly understood. But it should be possible to develop order-of-magnitude description of this process and gradually build up a body of supporting data which can lend credibility to the model.

In support of this viewpoint we reproduce below a comment made by Dr. S.E. Hrudey of the University of Alberta as a result of reviewing an early draft of this report.

"I believe that there is scope to demonstrate that your concept for a relatively simple model for fate in STPs is feasible based upon scoping of mechanisms and removal rates. I suspect for the majority of contaminants, some processes (i.e. volatilization) will so dominate others that the others can be ignored. That type of scoping exercise will certainly allow the model to condense to a fairly simple character for many contaminants. The scoping will also dictate where the most energy should be directed for gathering of more detailed data."

2.7.2 The Purpose of Models.

At this point it is perhaps useful to reflect on the nature of models, their complexity and purposes. We can only see the future of STP modelling dimly, but certain broad principles can be enunciated.

The most successful environmental models are probably the oxygen sag equation for rivers, the Gaussian air dispersion equations, and the phosphorus loading eutrophication models. In all cases the models are relatively simple and can be understood with little or no difficulty by practicing environmental and municipal engineers and other scientists. In many instances the models may be inaccurate or even erroneous but they provide a mathematical framework which is based on established physical, chemical or biological "laws" which enables discussion towards regulation to be focussed on quantities and issues of specific model applicability. When models are lacking, as in the case of effects of carcinogenic chemicals, discussion often degenerates into lengthy and inconclusive debates about intangibles such as "acceptable risk" or safety factors. It is preferable if the discussion can focus on numbers derived from a consistent and rational approach. Industry has accepted that the regulation of air emissions using Gaussian calculations to arrive at point-of-impingement concentrations is a valid, reasonable, and consistent approach. Models are always subject to criticism that they do not include one mitigating factor or another, but even the most obstructionist regulatee would not contemplate returning to the days of arbitrary setting of emission rates based on what may be regarded as from one point of view as "collective wisdom" - and from another as "arbitrary fickleness". The key point is that, despite its problems, the Gaussian method is viewed by industry as reasonable and consistent. It eliminates, or at least exposes, situations of excessive regulatory zeal on one hand and excessive emission on the other.

We thus argue that the MISA, STS model should also have these characteristics, at least to the extent that it is possible. It must be fairly simple and robust, yield results which seem to be intuitively reasonable and it must have been subjected to a validation procedure. If the model is not understood by all parties, especially industry and municipalities, it will be distrusted and effort will be devoted to discrediting the process and developing other, probably more arbitrary, methods of assessment.

If a model can be developed and made widely available, it enables industries and municipalities to conduct their own assessments and gauge in advance the MOE response. A proposal to discharge chemical X may thus never reach the Ministry because it can be determined in advance that such a proposal would be ill-fated. This "internalizing" of the regulatory decision is efficient and is emerging as the favoured approach in marketing new consumer chemicals and pesticides.

Another principle which was discussed at the June meeting, was that given the present rudimentary state of the art in STP modelling, the best strategy is to encourage several modelling efforts by different groups taking different perspectives. There would be periodic inter-calibration or comparison, preferably in a slightly competitive peer-review environment. In this way modellers will adopt the better features of each other's approaches, novel features will be encouraged, mistakes will be exposed (to the delight of the exposer and the chagrin of the exposee) and steady progress will be encouraged towards a few widely accepted models which may have different spheres of applicability.

The problem which we address later is to define courses of MOE/DOE action which will accelerate this process and enable an acceptable modelling system to be in place in 1989.

Development of highly complex models involving extensive computer coding and large quatities of input information is thus not favoured. Such models may have scientific value and may ultimately play a regulatory role, but not it is believed, by 1989. A basic problem in model development is whether the equations should be steady state and algebraic in nature or unsteady state and differential. If time variation of input and recycle proves to be an important determinant of treatability it may be necessary to develop unsteady state models. The current Environment Canada Dynamic STP project supervised by Dr. Melcer should shed some light on this issue. It is hoped that a relatively simple steady state model will be adequate.

3. APPROACHES TO PROTOCOL DEVELOPMENT.

3.1 Introduction.

From a consideration of what are judged to be feasible goals and the present state of the art it is suggested that the Ministry sponsor a number of studies which will provide information elements which can be combined ultimately in a decision support system. We identify and discuss these studies in this section. But first in the interests of clarity we present a scenario of the entire ultimate system.

3.2 The Protocol: a Scenario.

It is first useful to review the general background as documented in the MISA policy statement. It should be emphasised that this is the author's perception of the process, which may be in error because of misunderstanding or policy changes.

It is envisaged that for each chemical (specifically chemical X in this example) water quality criteria will have been developed in the form of Provincial Water Quality Objectives (PWQO). This objective will have been arrived at through a consideration of public health, aquatic life, wildlife and other short and long term water use considerations. For a specific lake or river, this concentration (say 1 ug/L) will be used to calculate an emission rate using data on stream flow, mixing, volatilization, sedimentation etc. This process could take the form of simple calculations or computer models. This emission rate (say 10 g/day) will then represent an amount which will result in 1 ug/L concentration. This emission rate and concentration must not be exceeded.

In parallel, or previously, an effluent monitoring effort will have been mounted to gather information about the amounts of chemical X which are being discharged in this region. This work will have been done by the industries or municipalities responsible for the relevant discharge. It is possible that there are total discharges of 50 g/day.

Environmental monitoring (as distinct from discharge monitoring) may then be appropriate to ensure that this discharge is indeed yielding concentrations of approximately 5 ug/L which obviously exceeds the PWQO of 1 ug/L.

The Ministry will also set "Best Available Technology Economically Achievable" (BATEA) effluent limits for each industrial and municipal sector, following the well established EPA approach. This process will involve defining and establishing municipal and industrial sectors, consideration of the candidate contaminants likely to be encountered in each sector and a review of treatment technology and costs. Ultimately performance levels will be defined in terms of concentration (e.g. mg/L), or mass loading (g/day), or load per unit of production. Consideration will be given to non-water impacts to avoid the mere transfer of the problem to other media such as air or land. It may be determined for example that 15 g/day is a BATEA effluent limit, the implication being that it is achievable at acceptable cost using available technology.

Comparison will then be made of the Water Quality limit (10g/day) the BATEA limit (15 g/day) and the prevailing value (50 g/day) and a decision made to reduce the limit to the smaller of the Water Quality and BATEA values, namely 10 g/day. How this limit is to be achieved is left to the discharger to decide.

The system will involve consultation at all stages. Limits may change with time in the light of new information about the fate and effects of chemicals, and the emergence of new treatment technologies.

In this scenario a municipality contributes most (40 g/day) of the 50 g/day and it is decided that this discharge should be reduced to 8 g/day. The municipal engineer thus faces the task of achieving this reduction by a combination of improved treatment, or more likely in the short term, reduction of source amounts. In this scenario it transpires that the total source discharge into the municipal sewage collection system is 200 g/day which translates into 40 g/day discharge to the receiving water. The fate of this 200 g/day is as follows.

(i)	loss in sewer systems	10 g/day	(5%)
(ii)	biodegraded in STP	100 g/day	(50%)
(iii)	sorbed to sludge and incinerated at STP	10 g/day	(5%)
(iv)	volatilized from the STP	40 g/day	(20%)
(v)	discharged to receiving water	40 g/day	(20%)
	total	200 g/day	(100%)

The municipal engineer obtains this information from the "Protocol" and is now able to approach those industries (and the public) responsible for the 200 g/day and seek reductions to approximately 40 g/day which could translate into an 8 g/day ultimate discharge. This assumes linear behaviour of the chemical in the system which may or may not be true. A model should assist in justifying this or other assumptions. Industries may choose to treat their waste on site instead of discharging to sewers, they may switch to other chemicals, implement recycling programs, or arrange for waste disposal elsewhere.

A similar approach can be used for new chemicals which are proposed for discharge. If the chemical is 99% biodegraded it will clearly be acceptable to discharge more of it than one which is only 5% degraded or removed.

The key point is that a Protocol must be available to estimate the fate of these chemicals in the sewage treatment system.

When using the Protocol, the engineer will presumably first define the subject chemical and obtain a profile of its relevant properties. One of two situations will then apply. If sufficient information is available the engineer will proceed with the protocol calculation. If insufficient information is available she will seek advice on likely values from the Ministry. These values may be obtained by expert judgement, consultation with experts, literature or data base search or experimental determination. This task of obtaining information should be central to the Ministry and will involve liaison with other agencies. It is unrealistic to expect the municipal engineer to have the time or experience to assemble or estimate these data.

The engineer will access a computer program which is already calibrated or validated with respect to the performance of the STS and STP in question i.e. it will have given a satisfactory description of treatment fate of selected chemicals. The chemical data will be entered and an output generated presenting a simple mass balance prediction. The tolerable amount of chemical input to achieve the desired output will be easily estimated. A full print out of all relevent data, assumptions and calculations will be provided for scrutiny by the engineer and those responsible for the discharge. There may be discussion about the validity of the assumed chemical solubility or degradability and if necessary experiments can be conducted to obtain more reliable data.

If the issue is contentious or potentially expensive it may be desirable to seek data on treatment fate of this chemical in this or other systems which can be used to validate (or otherwise) the results.

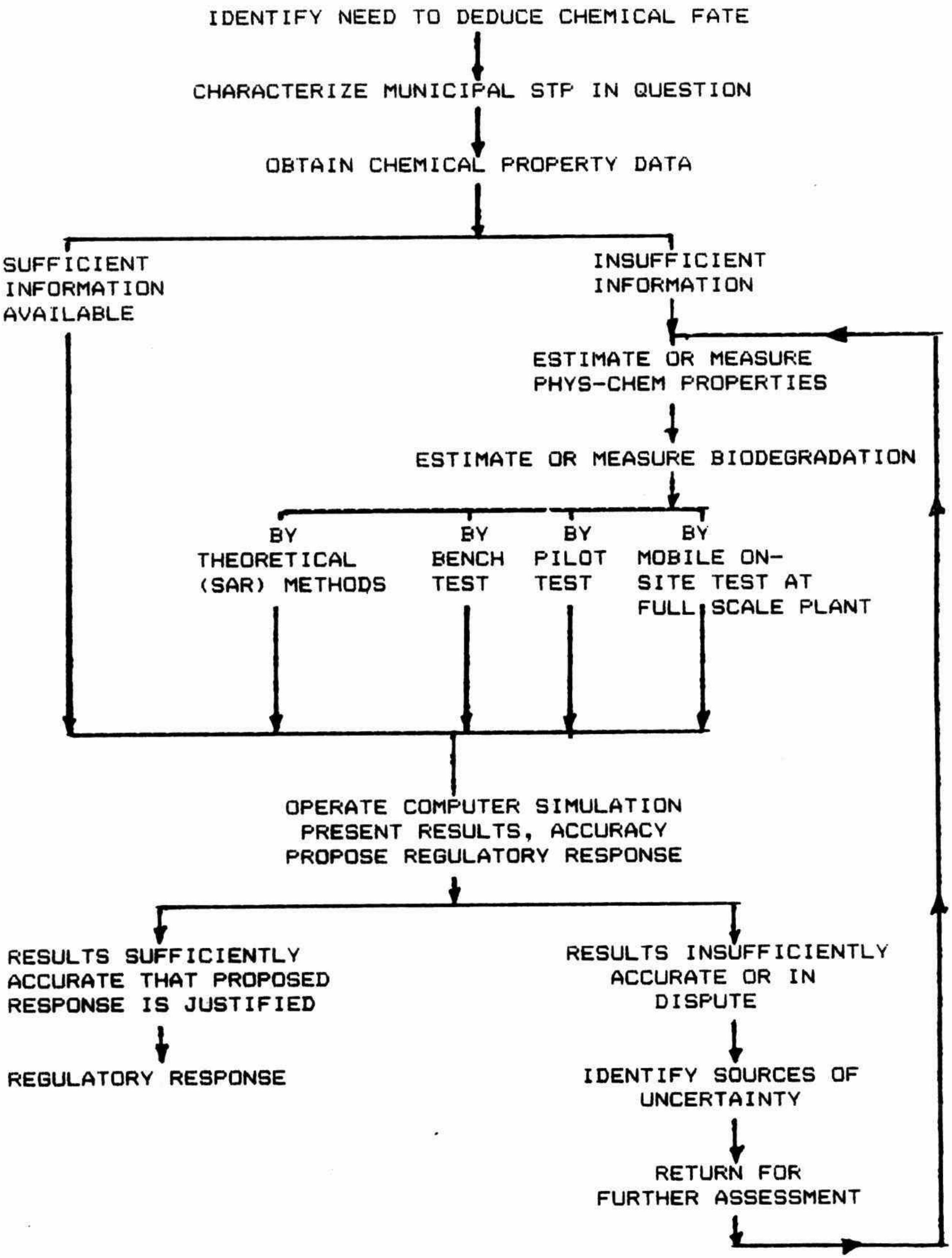
Our primary concern here is the mechanics of that Protocol.

A flowchart showing the sequences of events and the logic is given in Fig. 3.1.

3.3 Establishing the Protocol.

It is believed that such a protocol could be established in two to three years. It would have several features which will be obviously in need of refinement, and it is expected that it

FIGURE 3.1 PROTOCOL LOGIC DIAGRAM


IDENTIFY NEED TO DEDUCE CHEMICAL FATE
CHARACTERIZE MUNICIPAL STP IN QUESTION
OBTAIN CHEMICAL PROPERTY DATA
SUFFICIENT INFORMATION AVAILABLE
INSUFFICIENT INFORMATION
ESTIMATE OR MEASURE PHYS-CHEM PROPERTIES
ESTIMATE OR MEASURE BIODEGRADATION
BY THEORETICAL (SAR) METHODS
BY BENCH TEST
BY PILOT TEST
BY MOBILE ON-SITE TEST AT FULL SCALE PLANT
OPERATE COMPUTER SIMULATION
PRESENT RESULTS, ACCURACY
PROPOSE REGULATORY RESPONSE
RESULTS SUFFICIENTLY ACCURATE THAT PROPOSED RESPONSE IS JUSTIFIED
REGULATORY RESPONSE
RESULTS INSUFFICIENTLY ACCURATE OR IN DISPUTE
IDENTIFY SOURCES OF UNCERTAINTY
RETURN FOR FURTHER ASSESSMENT

will undergo continuous updating and improvement. Establishing the protocol will require a number of reviews and studies which will form a set of background documents, on which the final protocol can be established. The key background studies will involve:

1. Development of hazardous contaminants data base.
2. Biodegradability Assessment of hazardous contaminants.
3. Establishment of a list of bench-mark chemicals with properties.
4. Measurement and Modelling of hazardous contaminants in STPs. (consisting of three parts).
   - A. Acquisition of data concerning the performance of STPs.
   - B. Experimental determination of the partitioning and dynamics of selected hazardous contaminants in STPs.
   - C. Development and comparison of mathematical models of HC fate in STPs.
5. Fate of hazardous contaminants in sewer systems.
6. Project coordination.

4. THE STUDIES: TERMS OF REFERENCE.

4.1 Introduction.

This chapter contains a draft set of terms of reference for proposal. It is envisaged that each RFP will contain a common introductory statement prepared by MOE/DOE describing the general objective of the MISA program with reference to the MISA policy statement and, if desired, this report. This would be followed by a statement of all the tasks. In view of the linkages between tasks it may be desirable that all bidders receive all RFPs. It may be appropriate to go through a first screening to prepare a short list of bidders. This will give consultants the opportunity to form partnerships and create structures to manage the entire program with a network of subcontracts.

Considerable thought has gone into the formulation of these projects, but some splitting or combining, adding or deleting may be appropriate. The list and content should thus be viewed as a draft.

It should be noted that work on developing this list started in the summer of 1986. Late in 1986 the Ministry and Department issued Requests for Proposals and awarded contracts in several areas. It was decided, however, to proceed independently with this set of work statements. The reader is advised to seek information on the current status of such efforts by consulting the sponsors, or obtaining copies of the "Wastewater Technology Centre Newsletter" of Environment Canada. For example, the February 1987 issue contains a description of MISA studies relevant to studies 4 and 5 described later.

Figure 4.1 gives an approximate flowchart of the sequence of studies.

4.2 Project Descriptions.

4.2.1 Development of a Hazardous Contaminants Data Base.

The contractor will

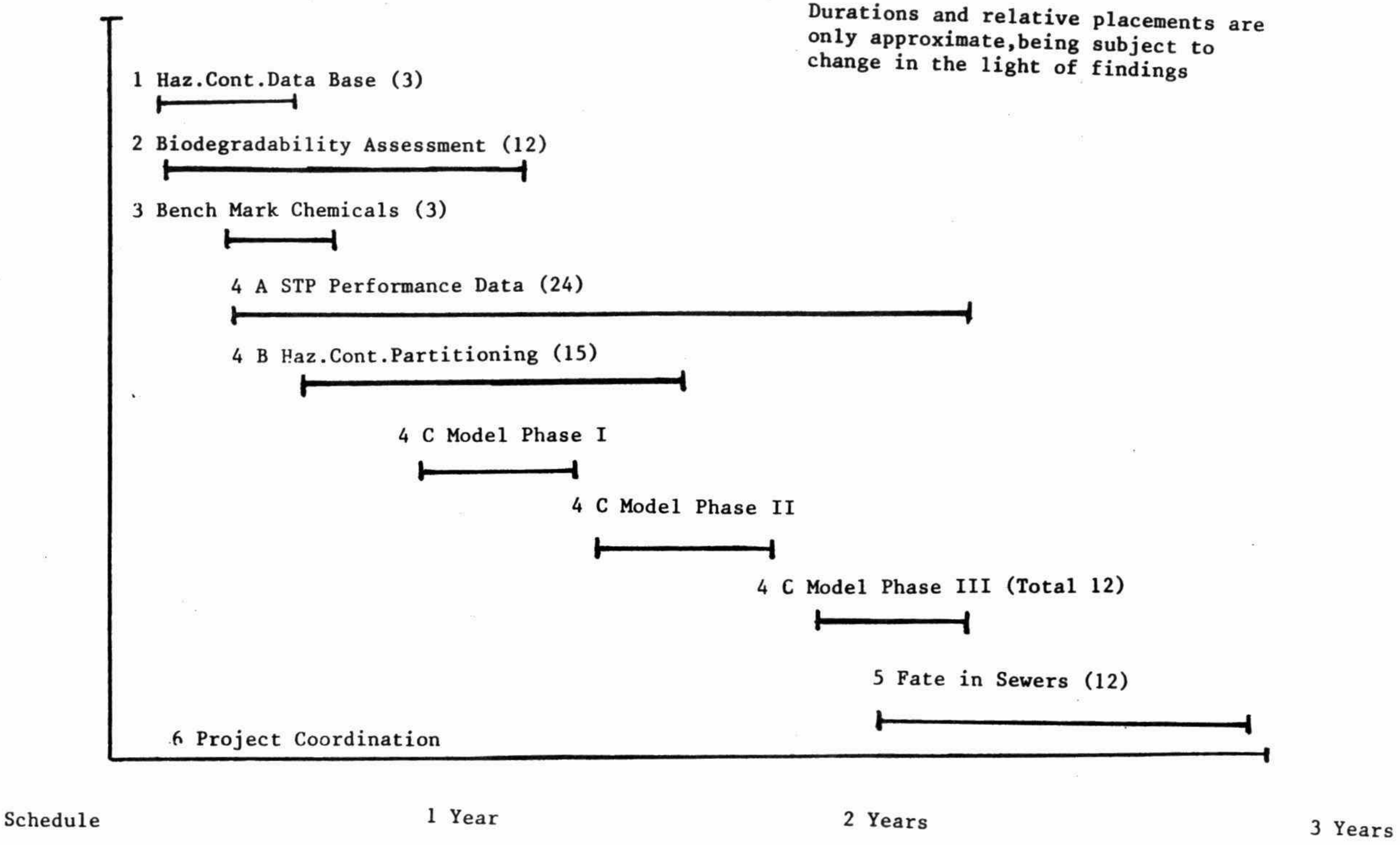
1. Review and report on existing data bases providing information about the properties and uses of hazardous contaminants, their availability, cost, coverage, accuracy, etc. This should include an account of methods used in other jurisdictions (e.g. U.S.EPA, Michigan, OECD etc.) to compile, modify and use such data. It should be consistent with the policies stated in the EMPL list. (MOE 1987).

2. In the light of the data demands for the protocol, compile a list of the essential and desirable data, the required and achievable accuracy for each element, and provide information about estimation procedures, and experimental determination methods cost and capabilities. Emphasis should be placed for the purposes of this protocol on methods of estimating biodegradability.

3. Identify other users in Canada who may wish to collaborate with, or have access to, such a data base. Consult with these users to determine their plans. This will include other Ontario Ministries and other parts of MOE, Federal and Provincial Governments, Industry and Universities and Research Organizations.

4. Recommend a system to MOE for the establishment of a

Figure 4.1 Bar Chart of the Projects



Durations and relative placements are only approximate, being subject to change in the light of findings database system by which municipal engineers and others can obtain reliable property data about contaminants.

5. Prepare a comprehensive report with recommendations.

Note.

It will be necessary to address issues such as updating, critical review or evaluation of data, the need for user training, the nature of electronic or other systems, manpower required and confidentiality.

Estimated Duration 3 months

(Note that other parts of MOE/DOE should wish to contribute to and collaborate with this project. The schedules of chemicals in the proposed Canadian Environmental Protection Act could influence this study. Other agencies such as the National Institutes of Health in the U.S. are contracting compilations of this type, thus contact should be made with this and similar groups).

4.2.2 Biodegradability Assessment of Hazardous Contaminants.

A major difficulty in assessing the treatability of chemicals is the prediction of their biodegradability. This project will result in a recommendation to the Ministry concerning appropriate methods. A review will be conducted and discussions held with experts covering the following topics.

(i) Status of structure-activity calculations (e.g. the Dearden method)

(ii) Bench scale tests (e.g. Tabak)

(iii) Stationary pilot scale test system (e.g. CCIW)

(iv) Use of mobile (trailer) pilot systems which can be taken to specific STPs for on-site testing.

(v) Approaches used in other jurisdictions, especially U.S.A.

The merits and demerits of each system will be discussed and a set of recommendations made to MOE for a tiered protocol which can be adopted to determine biodegradability quantitatively and in a format suitable for use in models and other assessments. The recommendations should take into account cost, capability, reliability, use by other jurisdictions and the issue of biotransformation vs mineralization.

Experimental testing of candidate systems will be undertaken by the contractor who will demonstrate the ultimate system(s) to MOE.

The report will contain full documentation of the system(s) such that it (they) can be used immediately. It will be appropriate to discuss limitations and research needs with a view to improving reliability at a later date.

Duration 12 months.

4.2.3 Establishment of a List of Bench-mark Chemicals with Properties.

In devising and testing the MISA protocol it will be necessary to have reliable data on a range of chemicals, possibly 30 to 50 in number which can be used to:-

(i) test the validity of models

(ii) be used as surrogate chemicals to predict the likely fate of similar chemicals, i.e. predict the fate of one chemical from another.

The contractor will develop a set of criteria for selection of benchmark chemicals and review these criteria with the Ministry and with experts in the field.

The contractor will then prepare a list of candidate chemicals which will satisfy these requirements (and as also detailed earlier in this report) and will document the following.

(i) critically reviewed, relevant property data.

(ii) treatability data or experience from lab, pilot or fullscale systems.

(iii) analytical protocols and cost of analyses. (This must be done in conjunction with the MOE Laboratory).

(iv) devise a system of "matching" other chemicals to this set to provide a statement of likely fate, i.e. similar in principle to the Biodose system described earlier in this report.

Estimated Duration 3 months

4.2.4 Measurement and Modelling of Hazardous Contaminant Fate of STPs.

This is a large multiphase project with the following components. It would probably involve several contractors.

Part A. Acquisition of Data Concerning the Performance of STPs.

The contractor will select (in conjunction with MOE and DOE) a list of 6 to 10 chemicals (as specified earlier) and obtain performance data on 5 Ontario STPs including

(i) influent concentrations

(ii) effluent concentrations in air, water and sludge

(iii) operating conditions i.e. volumes, flows, recycle rates, residence times, temperature, etc.

The resulting data should be complete and in a format suitable for testing mathematical models of HC fate in STPs.

It is envisaged that testing will occur over intensive periods of 10 days at 4 times of the year at 5 locations.

A comprehensive report will be written documenting and discussing the data and presenting mass balances

Duration 24 months

Part B. Experimental Determination of the Partitioning and Dynamics of Selected Hazardous Contaminants (HC) in STPs.

It is essential that any STP mathematical models be based on reliable information about HC fate in the various stages of a STP. The contractor will select (in conjunction with MOE) a set of 6 to 10 chemicals (mostly organics, but with perhaps 1 or 2 metals) covering a range of properties and determine total, dissolved or gaseous, and particle-associated concentration in the relevant vessels and streams of one "typical" STP. A mass balance will be established which can be used to calibrate mathematical models. This will be a detailed examination of one plant distinct from the multiplant proposal (4.2.4). Full plant operating conditions will be documented. The data will be interpreted to elucidate issues such as:-

- o extent of sorption and its dependence on chemical properties and solids content and nature.
- o extent of equilibration of air with water streams
- o effects of surfactants, electrolytes, pH etc.
- o influence of temperature
- o time variability

Duration 15 months

Part C. Development and Comparison of Mathematical Models of HC Fate in STPs.

A three-phase approach is envisaged.

Phase I

The contractor will document the available models, describing their structure, availability, data needs, extent of validation, current developments etc.

Comparisons will be of their theoretical bases, perceived deficiencies and strengths.

A similar set of input data should be run on all models and the results compared.

A report will be written recommending and justifying the adoption of one model, or a hybrid, or a novel system. The recommendation must be for a system which will be feasible by 1990.

Phase II.

Develop a modelling capability suitable for use by MOE staff and others including a description of all hardware and software, input needs, user training, expected accuracy, potential for improvement to include current developments, acceptability to other agencies (e.g. industry).

The model will be tested using sets of available STP performance data on selected chemicals and the results discussed.

A workshop/seminar will be held to describe and demonstrate the system to interested parties.

Phase III.

A peer-review of the final model system will be organized, ending in a meeting of experts and statement of opinion about reliability and future developments.

Duration 12 months

4.2.5 Fate of HCs in Sewer Systems.

It is believed that concentrations of many HC are substantially changed during their residence in sewer systems. An example is loss by evaporation. The contractor will review the literature and current research activities in this area (especially in U.S. EPA at Cincinnati) and report as follows.

(i) document the general nature, length, volume, retention time, venting practices of sewer systems in Ontario. This need not be a complete detailed inventory. It is intended to provide background on typical and extreme conditions.

(ii) report on those HCs which, it is suspected, are substantially changed in concentration or amount during residence in sewers.

(iii) obtain experimental data at 3 representative times of the year on water and air concentrations (as appropriate) for these chemicals in a number of sewer systems, with parallel documentation of flows etc.

(iv) report on these data and discuss the feasibility of, and need for, modelling or quantifying these changes and discuss the implications for worker safety, the extent of emissions with consideration of local air dispersion, reported public complaints etc.

Duration 12 months

4.2.6 Project Coordination.

The projects described in this statement will require careful coordination to ensure

(i) consistent selection of chemicals and their properties and analytical protocols with appropriate QA/QC

(ii) proper sequencing, reporting and information transfer at intermediate and final stages

(iii) that changes in project direction and supplementary projects necessitated by research findings are fully incorporated in all relevant projects and that all relevant parties are kept fully informed

(iv) that regular progress review and peer review meetings take place

(v) that proper liaison is maintained with MOE, DOE, EPA and other agencies and excessive or duplicating demands are not made of other agencies (especially the Waste Water Technology Centre at Burlington and U.S. EPA Cincinnati)

(vi) that a full protocol will be in place, tested and in operation, in early 1989.

The contractor will provide a management system to ensure that these needs are satisfied and that the overall project is fully coordinated

Duration 24 months

Note: The author is of the opinion that this project is best undertaken "in house" by Ministry staff, or by a contractor working "in house". Only in the event of severe staff shortage should it be contracted out.

4.3. Summary

The total cost of these 9 projects is estimated to in the range of $1.5 to $2.5 million. It is probable that other unanticipated studies, peer reviews, extensions etc. may contribute an additional $500,000.00 to give a planning total of $2 to $3 million.

A point worthy of re-emphasis is that it is essential that the analytical and sampling protocols for chemicals be carefully established and adhered to. Fortunately the Ministry has excellent inhouse capability in this area which can be exploited to ensure that the data generated are meaningful.

5. CONCLUSIONS.

In this report the author has attempted to review the large and complex issue of the fate of hazardous contaminants in municipal sewage collection and treatment systems. Emphasis has been on exposing the state-of-the-art in the science and technology in this area by reviewing the literature, conducting a workshop and discussing the findings of that workshop. The development of a protocol for describing and predicting the fate of chemicals in treatment systems has been discussed and a number of research studies have been identified and defined.

It is concluded that the development of such a protocol is both feasible and desirable. It would make a significant contribution to the control of toxic chemicals in the Ontario environment.

It is hoped that this document may serve to promote research towards the goal of controlling municipal discharges at acceptable levels and will be useful as a background document to those participating in this task.

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